

Available online at www.sciencedirect.com**ScienceDirect**

Procedia Structural Integrity 2 (2016) 541–548

Structural Integrity

Procediawww.elsevier.com/locate/procedia

21st European Conference on Fracture, ECF21, 20-24 June 2016, Catania, Italy

Internal and surface damage after electrochemical hydrogen charging for ultra low carbon steel with various degrees of recrystallization

A. Laureys^{a,*}, R. Petrov^{a,b}, K. Verbeken^a^a*Department of Materials Science and Engineering, Ghent University (UGent), Tech Lane Ghent Science Park – Campus A, Technologiepark 903, B-9052 Ghent, Belgium*^b*Department of Materials Science and Engineering, Delft University of Technology, Mekelweg 2, 2628 CD Delft, The Netherlands*

Abstract

An ultra low carbon (ULC) steel was subjected to electrochemical hydrogen charging to provoke hydrogen induced damage in the material. The damage characteristics were analyzed for recrystallized, partially recrystallized, and cold deformed material. The goal of the study is to understand the effect of cold deformation on the hydrogen induced cracking behavior of a material which is subjected to cathodic hydrogen charging. Additionally, charging conditions, i.e. charging time and current density, were varied in order to identify correlations between, on the one hand, crack initiation and propagation, and, on the other hand, the charging conditions. The obtained hydrogen induced cracks were studied by optical microscopy, scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD). Hydrogen induced cracks were observed to propagate transgranularly, independently of the state of the material. Deformed samples were considerably more sensitive to hydrogen induced cracking, which implies the important role of dislocations in hydrogen induced damage mechanisms.

Copyright © 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the Scientific Committee of ECF21.

Keywords: ULC steel; blisters; hydrogen induced cracking; EBSD; cold deformation

* Corresponding author. Tel.: +32-9-331-0418; fax: +32-9-264-5833.

E-mail address: aurelie.laureys@ugent.be

1. Introduction

Hydrogen entry into metals as occurring in everyday events, e.g. hydrogen formation from corrosion or applications such as arc welding (Griesche et al. (2014)), can be simulated experimentally by electrochemical charging of steel with hydrogen. Additionally, intensive electrochemical hydrogen charging can provoke surface and internal damage in a material (Pérez Escobar et al. (2011)), and, therefore, allows simulating the hydrogen induced cracking (HIC) behavior of metals. The internal pressure theory (Zapffe and Sims (1941)) (Tetelman and Robertson (1962)) clarifies the mechanism behind this damage formation. The theory states that HIC results from the formation of high pressure hydrogen gas bubbles in internal voids and microcracks in the material, when in contact with a hydrogen containing environment. The elevated pressure in such cavities causes plastic deformation of the surrounding lattice, as such reducing the effective fracture stress. The internal pressures can even rise to such levels that crack propagation occurs, even without the presence of an externally applied stress. If the abovementioned phenomenon occurs close to the sample surface, the high pressure pushes material upwards resulting in a surface blister (Pérez Escobar et al. (2011)). This phenomenon is referred to as blistering. The presented theory is only valid for high hydrogen fugacity environments, such as a high pressure hydrogen gas environment or extreme cathodic charging conditions.

Different blister initiation sites and initiation mechanisms have been proposed in literature for alloys charged with high-fugacity hydrogen introduced cathodically in acid solutions containing promoting species or by high pressure gas environment. Ren et al. (2008a) revealed that most nucleation sites (88%) for blisters are inclusions or second phase particles in steels. Wilde et al. (1980) found that blister cracking initiated at elongated manganese sulfide inclusions, glassy silicate inclusions, and massive niobium carbonitride precipitates in linepipe steels in sulfide environments. Ren et al. (2008b) and Griesche et al. (2014) studied high purity iron and found that the presence of a second phase is not a prerequisite for blister formation. Garofalo et al. (1960) stated that hydrogen induced propagation of internal cracks in iron and steel are promoted by hydrogen gas in voids or microcracks which may be formed by plastic deformation. Griesche et al. (2014) visualized small pores with diameters of $\sim 1 \mu\text{m}$ all over the hydrogen induced crack surfaces. These pores were located on grain boundaries, which are strong hydrogen traps. In summary, crack nucleation during hydrogen charging has been related to a localized concentration of hydrogen at suitable microstructural heterogeneities such as grain boundaries, second phase particles, microvoids and tangled dislocations. This localized concentration of hydrogen can then result in hydrogen recombination at these sites, resulting in the formation of hydrogen induced defects (Lee and Lee (1987)).

The trapping capacity of dislocations was studied by Pérez Escobar et al. (2012). They performed hot extraction measurements on hydrogen charged pure iron with increasing amounts of cold deformation. The hydrogen content increased with increasing deformation and, thus, also with increasing amount of dislocations. If samples were held 1h at low pressure after hydrogen charging and prior to hot extraction, the difference in hydrogen content was no longer detected. This result indicates that dislocations are weak traps containing only diffusible hydrogen, which readily diffuses out of the material when the sample is held in vacuum for 1h. The weak trapping ability of dislocations was also confirmed by Young and Scully (1998), who studied hydrogen embrittlement in pure aluminum. Choo and Young Lee (1983) found that the apparent hydrogen diffusivity decreases as the degree of cold deformation increases, which was attributed to the increase in dislocation and microvoid density.

Numerous parameters influence the blister formation in materials exposed to a hydrogen enriched environment, as for instance during electrochemical charging. Panagopoulos et al. (1998) studied hydrogen induced cracking and blistering in α -brass and found that the severity of cracking on the specimen's surface, the diameter and area fraction of blisters increases with the charging current density, when charged electrochemically. Blisters formed preferentially along grain boundaries at low current densities, as such resulting in intergranular cracking. When working at higher current densities cracks begin to propagate across grains or along characteristic slip lines, resulting in transgranular cracking. The charging time equally had an effect on the blister behavior in α -brass. No hydrogen cracks appeared on the specimen surface for short charging times. A critical hydrogen concentration should be reached in a trap for a hydrogen crack to form (Pressouyre (1982)). More recently, Pérez Escobar et al. (2011) have equally illustrated the effect of current density on the occurrence of blisters on the specimen surface. They stated that at higher current densities, a larger amount of blisters form, while the size decreases. Condon and Schober (1993) stated that the probability for blistering with hydrogen introduction is increased if: i) target materials have a low

solubility for hydrogen, ii) the sample is held at low temperature, and iii) in a very high hydrogen fugacity environment.

A lack of information concerning the effect of deformation on blister and internal damage formation exists. The current study analyzes the blistering behavior of ultra low carbon (ULC) steel with varying degrees of deformation, i.e. recrystallized, partially recrystallized and cold deformed material. Varying charging conditions, i.e. charging time and current density, were applied during cathodic electrochemical hydrogen charging. A surface and cross section analysis was carried out in order to characterize the formed blisters.

2. Experimental procedure

The hydrogen induced cracking behavior of an ULC steel with a chemical composition of 214 ppm C, 88 ppm N, 38 ppm S, 73 ppm P, 0.25 mass% Mn, 0.002 mass% Ti, 0.047 mass% Al was studied. The material consisted of ferrite grains, which contain a limited amount of hydrogen trapping site types, i.e. grain boundaries, dislocations and microvoids. Three microstructural states were tested: (1) 60% reduced by cold deformation, (2) partially recrystallized, and (3) fully recrystallized material. The corresponding microstructures are illustrated in Fig. 1. The recrystallized microstructure exhibited an average grain size of 14 μm .

Samples with a geometry as illustrated in Fig. 2 were processed out of the different sheets of material. The long diameter of the oval corresponds to the rolling direction of the plates. The thickness of these samples was 1 mm. Such geometry was selected, because it allows fast hydrogen charging due to the relatively large surface to volume ratio.

Hydrogen charging of the samples was performed by cathodic charging at room temperature using a 1 g/L of thiourea in 0.5 M H_2SO_4 electrolyte. Thiourea was added as a poison in order to promote hydrogen atom absorption into the metal. Different charging currents (2.5, 5, 10, and 20 mA/cm^2) and charging times (30', 2 h, 1 day, 2 days, and 4 days) were combined.

Surface analysis of the charged samples was performed by optical microscopy. Such type of analysis allows assessing the blister presence, size, and morphology. In order to obtain information concerning the internal structure of the charged samples and more specifically of the observed blisters, cross sections were taken. These cross sections

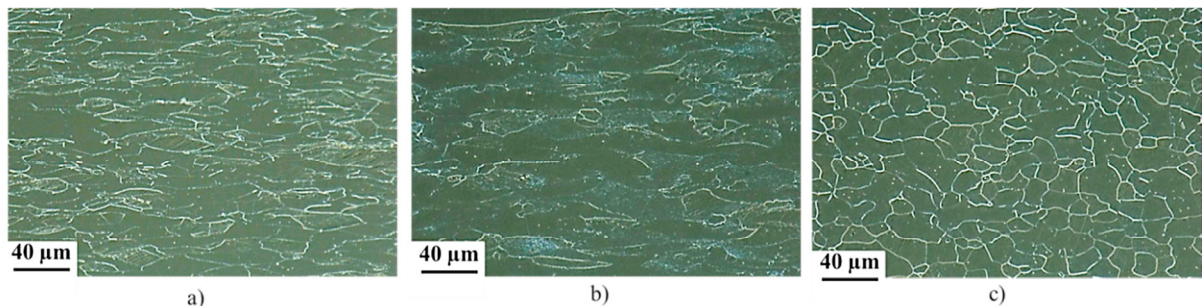


Fig. 1. Dark field optical microscopy images of the microstructure of a) cold deformed, b) partially recrystallized, and c) recrystallized ULC steel.

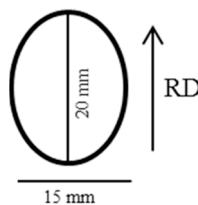


Fig. 2. Sample geometry.

were metallographically prepared by grinding with SiC papers and polishing with diamond paste (up to 1 μm) and finally etching with Nital 2% for 10s. First, the prepared surfaces were investigated by optical microscopy, followed by a scanning electron microscopy (SEM) investigation of the internal damage and electron backscatter diffraction (EBSD) of the most interesting features. For EBSD measurements the specimens required an additional mechanical polishing step with colloidal silica (0.04 μm) long enough to remove the layers affected by polishing with coarser particles. The SEM used for making the EBSD measurements was a FEI Quanta 450 with field emission gun (FEG). EBSD data was acquired at 20 kV acceleration voltage, emission current of 200 μA , specimen tilt of 70° and a scan step size of 0.25 μm on a hexagonal scan grid. TSL-OIM Data Analysis V6.1 software was used for post processing and analysis of the orientation data.

3. Results and discussion

Surface imaging by optical microscopy was carried out in order to analyze the blister distribution, sizes, and morphology. Blister formation and morphology for the three materials were compared for hydrogen charging at a charging current of 5 mA/cm^2 for 2 days. The evolution of blistering in time and for different charging current densities was studied for all materials, but will be discussed only for cold deformed material, since the global trends were equal for the different microstructural states of the material. Finally, SEM and EBSD were carried out on cross sections of blistered material.

Each microstructural state exhibited a different behavior when in contact with hydrogen. When the three materials were charged at 5 mA/cm^2 for two days, different amounts of blisters, blister sizes and shapes were observed (Fig. 3). The blistering behavior varied strongly between recrystallized and cold deformed material, while partially recrystallized material showed intermediate behavior, exhibiting characteristics of both extremes. With an increasing fraction of deformed microstructure, an increasing number of blisters formed and blister sizes equally rose. Additionally, a larger range of blister sizes was encountered in cold deformed ULC steel, with blisters covering a major part of the sample surface. Plastically deforming the material leads to the formation of dislocations and microvoids in the ferrite matrix, as such increasing the hydrogen trap density of the material (Pérez Escobar et al. (2012)). Hydrogen atoms can recombine to hydrogen gas in these specific locations (Garofalo et al. (1960)), which has a large impact on the blister initiation and propagation process. Their presence clearly facilitates blistering, making materials with a certain amount of deformation more sensitive to hydrogen induced cracking.

When considering the blister morphology in more detail (Fig. 4), several differences are observed. First, the blister's shape evolves from clearly delineated domes with an overall circular or oval shape for recrystallized material to less clearly defined blisters often only half emerging from the surface for deformed material. Blister caps of larger blisters are often covered with thin cracks. Second, the phenomenon of blisters on blisters was observed on the partially recrystallized and cold deformed samples. This phenomenon leads to a strongly non-homogeneous

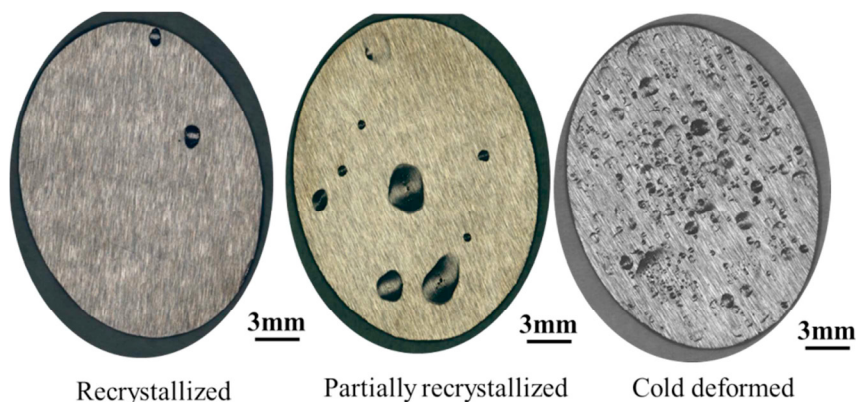


Fig. 3. Recrystallized, partially recrystallized and cold deformed ULC steel charged at 5 mA/cm^2 for 2 days.

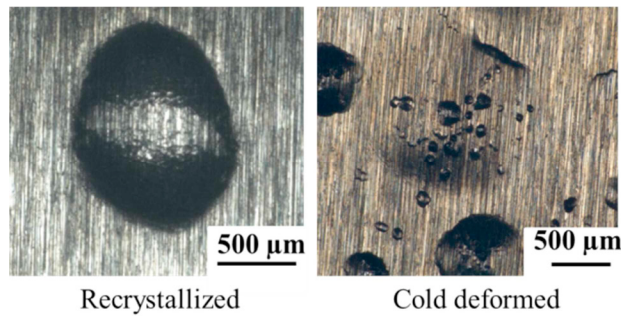


Fig. 4. Blister morphology of recrystallized and cold deformed ULC steel.

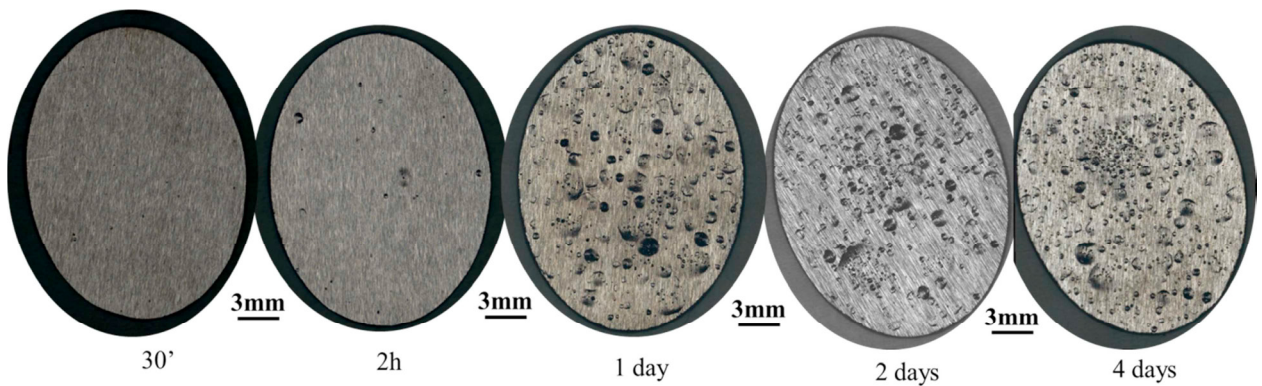


Fig. 5. Blister evolution in time for cold deformed ULC steel charged at 5 mA/cm².

blistering pattern on the surfaces of deformed ULC steel. The smaller blisters seem to concentrate mostly on larger blisters and in between these regions the density of small blisters is considerably lower. In material, that contains a certain fraction of deformed microstructure, blister initiation seems to occur preferably on previously existing blisters.

Fig. 5 shows the blister evolution in time for cold deformed ULC steel charged at 5 mA/cm². Blistering starts with the formation of numerous small blisters (<50 μm). Longer charging times result in the appearance of larger blisters and simultaneous formation of small blisters. After 4 days of charging very large blisters (>4500 μm) appear in combination with numerous small and medium sized blisters. Such trends were observed for all three materials.

Additionally, samples were charged at 2.5, 10 and 20 mA/cm² for 2 days in order to assess the effect of the charging current on the blistering characteristics (Fig. 6). The number of blisters increased strongly with higher

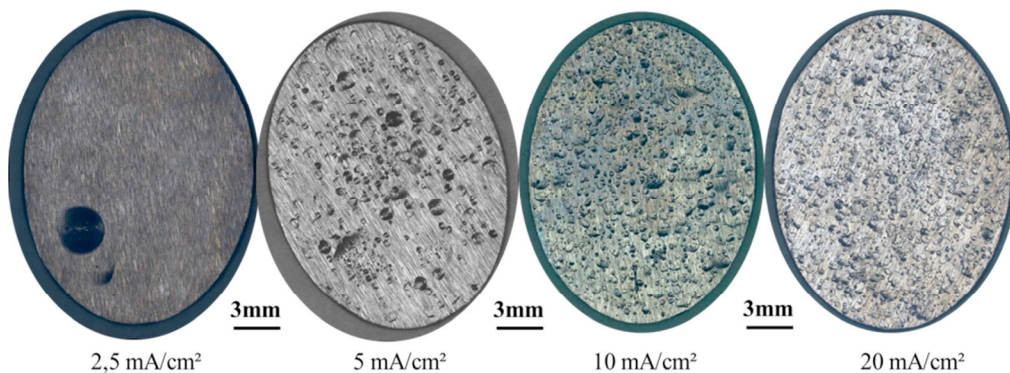


Fig. 6. Cold deformed ULC steel charged at various current densities for 2 days.

current densities. The blister size increased up to 5 mA/cm² followed by a decrease for higher current densities. This was again observed for the three materials. The phenomenon of blisters on blisters seems to diminish at higher current densities, leading to a more uniform blister distribution on the surface. The blister shape evolves from well delineated domes to rather low plateau-like elevations with jagged edges. Higher current densities seem to shift the more favorable process from blister growth to blister initiation. More hydrogen is simultaneously incorporated in the material, activating more initiation locations instantaneously.

Multiple cross sections were taken from all charged samples in order to analyze the internal hydrogen induced damage. Overall, it was observed that if no blisters were present on the sample surface, no internal cracks were found in the interior of the material, which indicates that blister formation at the surface is more favorable than crack formation in the bulk of the material. In Fig. 7, the cross section of a blister found on the recrystallized material charged at 5 mA/cm² for 2 days is illustrated. The internal crack grew parallel to the rolling plane and to the sample surface, while crack tips deflected toward the sample surface. The observed crack actually consisted out of numerous thin cracks branching and connecting again, staying within a certain region as to form a sort of larger crack entity. As such, grains or parts of grains are enclosed in the crack entity. These observations equally account for cold deformed and partially recrystallized samples.

Fig. 8 shows a ND inverse pole figure, on which one can see that the crack tip clearly propagates transgranularly. This observation was equally made for the other two materials. The enclosed material in the crack entity was strongly deformed, which is indicated by the high misorientations observed in these regions. Additionally, the crack entity is surrounded by locally increased misorientations. These two aspects are likely a result of the pressure build-up occurring in the cracks due to the hydrogen accumulation, as is the proposed hydrogen induced cracking mechanism by the internal pressure theory (Zapffe and Sims (1941)) (Tetelman and Robertson (1962)). The pressure build-up leads to plastic deformation of the surrounding material, resulting in local misorientations.

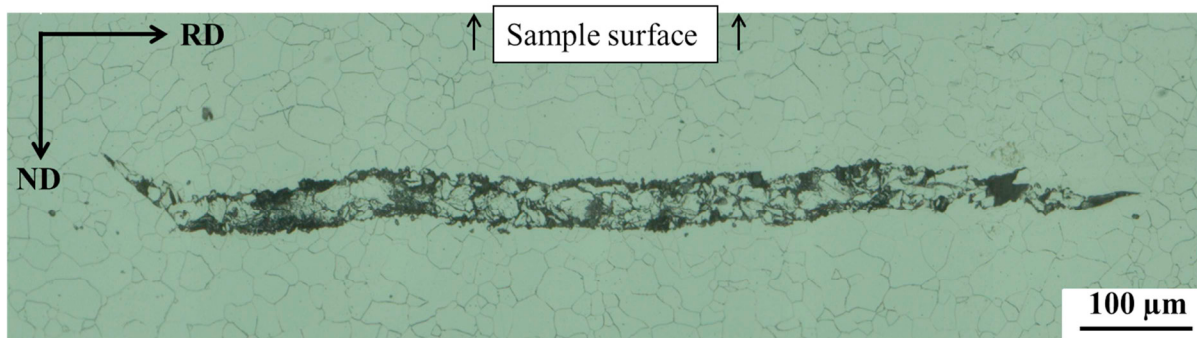


Fig. 7. Cross section of a blister in a recrystallized ULC steel charged at 5 mA/cm² for 4 days.

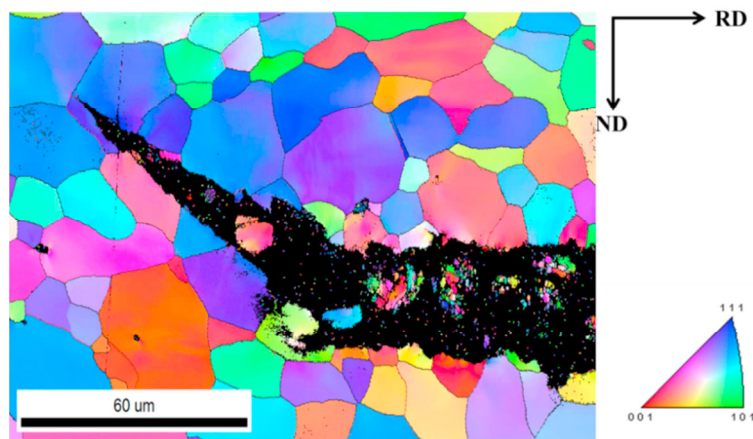


Fig. 8. ND Inverse pole figure of an internal crack in recrystallized ULC steel charged at 5 mA/cm² for 4 days.

4. Conclusions

A ULC steel with varying amounts of recrystallization, i.e. fully recrystallized, partially recrystallized, and cold deformed material, was subjected to extreme electrochemical hydrogen charging to provoke hydrogen induced damage in the material. The formation kinetics differed remarkably for cold deformed and recrystallized material. The deformation induced defects in the material clearly play a very important role in the initiation and propagation process of blisters. Also, the morphology of blisters depends on the state of the material, i.e. an increased fraction of deformed microstructure is accompanied by a flattening of blisters.

Increasing charging times resulted in an increase of the amount of blisters, which was also the global trend for increasing current densities. Additionally, the mean blister size increased with time, while it decreased with increasing current densities. Higher current densities seem to shift the more favorable process from blister growth to blister initiation. These trends were equal for all the materials.

Cross sections of the three materials showed that the hydrogen induced cracks are strongly branched, with each blister consisting of a large entity of thin, branching cracks. The hydrogen induced cracks propagated dominantly transgranularly. Additionally, high misorientations were observed within and along the hydrogen induced cracks. This observation can be considered as a confirmation of the internal pressure theory.

Acknowledgements

The authors wish to thank the Special Research Fund (BOF), UGent (BOF10/ZAP/121) and the Agency for Innovation by Science and Technology in Flanders (IWT) for support (Project nr SB141399).

References

- Choo, W.Y., Young Lee, J., 1983. Effect of cold deformation on the hydrogen trapping phenomena in pure iron. *Metallurgical Transactions A* 14, 1299-1305.
- Condon, J.B., Schober, T., 1993. Hydrogen bubbles in metals. *Journal of nuclear Materials* 207, 1-24.
- Garofalo, F., Chou, Y.T., Ambegaokar, V., 1960. Effect of hydrogen on stability of micro cracks in iron and steel. *Acta Metallurgica* 8, 504-512.
- Griesche, A., Dabah, E., Kannengiesser, T., Kardjilov, N., Hilger, A., Manke, I., 2014. Three-dimensional imaging of hydrogen blister in iron with neutron tomography. *Acta Materialia* 78, 14-22.
- Lee, J.-L., Lee, J.-Y., 1987. The effect of lattice defects induced by cathodic hydrogen charging on the apparent diffusivity of hydrogen in pure iron. *Journal of Materials Science* 22, 3939-3948.
- Panagopoulos, C.N., El-Amoush, A.S., Agathocleous, P.E., 1998. Hydrogen-induced cracking and blistering in alpha-brass. *Corrosion Science* 40, 1837-1844.
- Pérez Escobar, D., Miñambres, C., Duprez, L., Verbeken, K., Verhaege, M., 2011. Internal and surface damage of multiphase steels and pure iron after electrochemical hydrogen charging. *Corrosion Science* 53, 3166–3176.
- Pérez Escobar, D., Depover, T., Duprez, L., Verbeken, K., Verhaege, M., 2012. Combined thermal desorption spectroscopy, differential scanning calorimetry, scanning electron microscopy and X-ray diffraction study of hydrogen trapping in cold deformed TRIP steel. *Acta Materialia* 60, 2593-2605.
- Pressouyre, G.M., 1982. In: C.G. Interrante, G.M. Pressouyre (Eds.), *Current solutions to hydrogen problems in steels*. ASM, Metals Park, OH, pp. 18.
- Ren, X., Chu, W., Li, J., Su, Y., Qiao, L., 2008. The effects of inclusions and second phase particles on hydrogen induced blistering in iron. *Materials Chemistry and Physics* 107, 231-235.
- Ren, X.C., Zhou, Q.J., Shan, G.B., Chu, W.Y., Li, J.X., Su, Y.J., Qiao, L.J., 2008. A nucleation mechanism of hydrogen blister in metals. *Metallurgical and Materials Transactions* 39A, 87-97.
- Tetelman, A.S., Robertson, W.D., 1962. The mechanism of hydrogen embrittlement observed in iron-silicon single crystals. *TRANS TMS-AIME* 224, 775-783.
- Wilde, B.E., Kim, C.D., Phelps, E.H., 1980. Some observations on the role of inclusions in the hydrogen induced blister cracking of linepipe steels in sulfide environments. *Corrosion* 36, 625-632.
- Young, G.A., Scully, J.R., 1998. The diffusion and trapping of hydrogen in high purity aluminium. *Acta Materialia* 46, 6337-6349.

Zapffe, C., Sims, C., 1941. Hydrogen embrittlement, internal stress and defects in steel. TMS-AIME 145, 225-232.